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# An Overview of Progress Made Toward Resolving Priority One Safety Issues: Fiscal Year 1992

H. Babad

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Westinghouse
Hanford Company
P.O. Box 1970
Richland, Washington 99352

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Prepared by: ______________________ 12/15/92

H. Babad
Advisory Chemist

Date

Approved by: ______________________ 12/15/92

C. DeFigh-Price, Deputy Director
Waste Tank Safety Program

Date

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# AN OVERVIEW OF PROGRESS MADE TOWARD RESOLVING PRIORITY ONE SAFETY ISSUES: FISCAL YEAR 1992

**H. Babad**

## ABSTRACT

*High-activity radioactive waste has been stored in large underground storage tanks at the U.S. Department of Energy's Hanford Site in eastern Washington State since 1944. Since then, more than 227,000 $m^3$ (60 Mgal) of waste have accumulated in 177 tanks. The caustic waste forms consist of many different chemicals and include liquids, slurries, saltcakes, and sludges. A number of safety issues have been raised about these waste forms, and resolution of these safety issues is a top priority of the U.S. Department of Energy. The Waste Tank Safety Program has been established to resolve tank waste high-priority safety issues at the Hanford Site.*

*This report provides a brief general summary of the accomplishments made toward resolving the following safety issues associated with Hanford Site high-activity single and double-shell waste tanks:*

- *Flammable gas tanks*
- *Ferrocyanide containing tanks*
- *Organic tanks*
- *Tank vapor concerns*
- *High-heat tanks.*

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## CONTENTS

## LIST OF TERMS

| | |
|---|---|
| DOE | U.S. Department of Energy |
| DST | double-shell tank |
| FY | fiscal year |
| GRE | gas release event |
| NOAS | noxious odor advisory system |
| PNL | Pacific Northwest Laboratory |
| R&D | research and development |
| SAIC | Science Applications International Corporation |
| SST | single-shell tank |
| TOC | total organic carbon |
| USQ | unreviewed safety question |
| WHC | Westinghouse Hanford Company |

# AN OVERVIEW OF PROGRESS MADE TOWARD RESOLVING PRIORITY ONE SAFETY ISSUES: FISCAL YEAR 1992

## 1.0 INTRODUCTION

High-activity radioactive waste has been stored in large underground storage tanks at the U.S. Department of Energy's (DOE) Hanford Site in eastern Washington State since 1944. Since then, more than 227,000 $m^3$ (60 Mgal) of radioactive waste have accumulated in 177 tanks. These caustic waste forms consist of many different chemicals and include liquids, slurries, saltcakes, and sludges. A number of safety issues have been raised about these waste forms, and resolution of these safety issues is a top DOE priority. The Waste Tank Safety Program has been established to resolve these high-priority safety issues.

Extensive management controls are employed to ensure that the waste tanks in question continue to be maintained in a safe manner. Comprehensive monitoring, characterization, and applied/basic research efforts have been initiated to support resolution of issues and to prevent creation of future problems associated with potentially incompatible waste forms. Safety efforts will also support actions related to the planned retrieval and disposal of the waste forms in the storage tanks. These efforts will provide the basis for safe near-future remediation of the waste tanks on an as-needed basis and will define the envelope of safety to support the disposal of all high-level waste forms in Hanford Site tanks. In addition, the Waste Tank Safety Program receives considerable DOE-Headquarters and third party oversight, which provide a mechanism for ensuring that actions taken under the program are appropriately reviewed.

The following priority one safety issues are reported on in this document:

- Flammable gas tanks
- Ferrocyanide containing tanks
- Organic tanks
- Tank vapor concerns
- High-heat tanks.

The following sections are organized to provide a brief general summary of the accomplishments made toward resolving the safety issues associated with Hanford Site high-activity single and double-shell waste tanks.

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# 2.0 THE FLAMMABLE GAS TANKS

## 2.1 INTRODUCTION

Of the 177 high-level waste tanks on the Hanford Site, 23 tanks have been identified as having a potential to generate and release hydrogen gases in an episodic manner. Efforts were initiated in 1990 to (1) ensure the tanks were being operated safely, (2) conduct a characterization of the waste, and (3) develop approaches for mitigating the release of hydrogen-containing gases. The focus of the efforts has been on tank 241-SY-101 (101-SY) because this tank has been shown to be the most active tank for the cyclic release of gases. Tank 101-SY vents gases about every 100 days. The major components have been determined to be hydrogen (fuel), nitrous oxide (oxidizer), and nitrogen in about equal proportions (Reynolds and Babad 1992). In some cases the venting has resulted in mixtures that are above the lower flammability limit. In several of the recent release cycles in tank 101-SY the gas release event (GRE) created transient pressures in the vapor slightly above atmospheric pressure. Dome vapor space pressure in ventilated tanks is usually, for radiation protection consideration, kept at a small negative pressure.

Because of this cyclic behavior, Westinghouse Hanford Company (WHC) limits intrusions into the tank to a predefined "window of safety" that starts after a GRE. The length of the window is set by the amount the surface level drops. For example, a drop of 12.7 to 15.2 cm (5 to 6 in.) will open up a 20-day window. A 15.2-cm (6-in.) or greater drop will open a 30-day or longer window. Nonsparking tools and use of electrical bonding techniques on all equipment items are used around flammable gas tanks. So-called "normal" activities are limited to surveillance. Special safety and environmental analysis documents are prepared for all work that is performed inside the tank, and the analyses are extensively peer reviewed.

Although 22 other tanks are also suspected of potentially containing smaller accumulations of hydrogen or other flammable gases, this report focuses only on tank 101-SY. There is a significant difference in behavior (e.g., gas release quantity and intensity) between tank 101-SY and the other 22 tanks. Two other double-shell tanks (DSTs), tank 103-SY and tank 104-AN, also have a demonstrated cyclic release of gas. However, their GREs are much less dynamic then that in tank 101-SY. None of the other 20 tanks show any evidence of cyclic GREs. Evidence of gas release, surface level behavior, and knowledge of the other tank contents suggests a much lower likelihood of potentially dangerous gas concentrations in the other tanks.

In the course of a general review, concern for this cyclic behavior was heightened in 1989, when it was recognized that the gases generated and released included a mixture of hydrogen (a fuel) and nitrous-oxide (an oxidizer) that was flammable, indeed explosive at sufficient levels of concentration, even if not mixed with air. This condition had not been considered in previous safety analysis documents. Because the potential consequences of the presence of an oxidizer (nitrous oxide) and fuel (hydrogen) in the gases generated in tank 101-SY had not been covered in previous safety analyses, the condition was designated an unreviewed safety question (USQ). However, documented safety analyses previously had taken into account the generation and release of flammable concentrations of hydrogen gas into the air-filled dome space.

Additional technical background information on this issue is available in a report by the Pacific Northwest Laboratory (PNL) Science Panel (Reynolds et al. 1991).

Major program participants include the following:

| Program participant | Program role |
|---|---|
| Westinghouse Hanford Company | Program management, waste tank monitoring and characterization, waste tank dome space modeling, engineering studies, safety and environmental analysis, waste characterization, and actual radwaste degradation and gas evolution studies. |
| Pacific Northwest Laboratory | Applied research and development on gas generation, waste system physical modeling, waste energetics, analytical methods development, waste aging studies, and waste characterization support. |
| U.S. Bureau of Mines | Nitrous oxide, hydrogen and air combustibility studies. |
| Los Alamos National Laboratory | Safety analyses for mitigation and development of instrumentation to support mitigation testing. |
| Argonne National Laboratory | Radioactive gas generation and complexant degradation waste simulant studies. |
| Georgia Institute of Technology | Nonradioactive chemically induced gas generation and complexant degradation simulant studies. |
| Numerical Applications, Inc. | Development of the GOTH code and application of the code to mitigation test related modeling. |

## 2.2 SUMMARY FISCAL YEAR 1992

A significant portion of the activities of the Waste Tank Safety Program has been jointly directed at the characterization of the gases that are released from tank 101-SY and at the definition of the mechanism(s) for the production, retention, and release of these gases. The main emphasis of the program during the last fiscal year (FY) was to (1) characterize the GRE; (2) analyze the data obtained from the recent GREs, historical data, and from actual waste sampling activities; and (3) interpret the results obtained from items 1 and 2, as well as from laboratory studies to gain a detailed understanding of mechanisms for the formation and storage of the gases. That knowledge was then applied toward mitigating the risks from tank 101-SY. Such information can and will be applied to the assessment of the other flammable gas tanks, thus providing assurance that waste compatibility is assured during retrieval efforts (which are a part of the Tank Waste Remediation System program). This information will also provide detailed information to the WHC organic program on the fate of complexants in Hanford Site high-activity waste tanks.

As described in the following list and table, major quantities of past and newly generated information on tank 101-SY were collected, compiled, analyzed, and published.

The key FY 1992 achievements are listed below.

- The concern for a secondary crust burn in tank 101-SY was closed.
- A mitigation strategy for tank 101-SY was developed and is being implemented.
- Experimental bounds for the lower flammability limit of nitrous oxide, hydrogen, and nitrogen in a wet environment were developed by the U.S. Bureau of Mines.
- Extensive characterization data on the chemical and physical properties of the waste in tank 101-SY were obtained.
- Detailed studies with waste simulants paralleled by extensive modeling have expanded our understanding of gas generation, retention, and release in tank 101-SY. (This new data formed the basis for the mitigation efforts that are underway.)
- A report was issued on USQ resolution strategies containing extensive background material on tank 101-SY (Simpson et al. 1992).

A more detailed summary of accomplishments is tabulated below.

| Information | Preliminary conclusion or result |
|---|---|
| Crust burn issue closed | A detailed analysis that combined data from core samples, in-tank observations, and kinetics and energetics studies on both simulated and actual waste led to the "closure" of the issue of there being a potential for a crust burn in tank 101-SY (Fox et al. 1992). |
| Development of a mitigation strategy (101-SY) | Mitigation strategies for tank 101-SY were developed that focused on the combination of waste mixing (jet mixer pump), heating and/or dilution of the waste, and/or the user of ultrasound or sonification techniques to mix or force gas bubble release (Babad et al. 1992).<br><br>An in-tank test of the jet pump is nearing startup and detailed development of an enclosed housing for an in-test of the other mitigation methods is under development (Lentsch 1992).<br><br>Analytical instrumentation to support pump testing has been installed in the tank.<br><br>Test chamber design to evaluate ultrasound, dilution, and heating concepts is 90 percent complete. |
| Estimate of the lower flammability limits for gases produced in tank 101-SY | Work by the U.S. Bureau of Mines provided detailed experimental data on the behavior of nitrous oxide, hydrogen, and air under a variety of conditions that simulated the potential condition in tank 101-SY (Cashdollar et al. 1992). |
| SY Tank Farm ventilation improvements | SY Tank Farm ventilation system was enhanced and an inlet filter was added to tank 101-SY. |

| Information | Preliminary conclusion or result |
|---|---|
| Tank monitoring (tank 101-SY) | The following added and enhanced capability to monitor tank 101-SY:<br>• Measured quantity of gases generated in tank<br>• Identified gases generated in tank both between and during a GRE<br>• Installed video camera to enhance ability to observe tank phenomena<br>• Installed radar gauge to provide additional surface measurements<br>• Installed an additional thermocouple tree to provide better temperature data. |
| Tank modeling | The following are significant new understandings of the behavior of tank 101-SY, which will also serve as a model for the analysis of 103-SY and 104-AN (Reynolds et al. 1992, Schulz and Strachan 1992, Strachan 1991, Strachan 1992a, and Strachan 1992b).<br>• Enhanced the capability to model changes in dome space during a GRE using both GOTH[1] and TEMPEST[2] codes.<br>• Developed a suite of rollover and mixing models to analyze tank behavior before, during, and after a GRE.<br>• Analyzed the thermal characteristics of tank 101-SY. |
| Waste characterization | A variety of surface and two full length core samples from tank 101-SY were obtained. Extensive analysis of the waste to determine their chemical and physical properties was completed (Herting et al. 1992a, Reynolds 1992, Herting et al. 1992b).<br><br>Dilution and heating studies on actual waste were also completed. |

| Information | Preliminary conclusion or result |
|---|---|
| Studies with waste simulants | Detailed studies, both under radiolytic conditions and using nonradioactive simulants, are underway at PNL, Georgia Institute of Technology, and Argonne National Laboratory. This applied research and development (R&D) effort is focused on gaining an understanding of the gas generation, retention, and release mechanisms in tank 101-SY. Although the laboratories have not been able to replicate the rates and ratios of actual gas generation in tank 101-SY or to identify the actual physical mechanism for gas retention, the information obtained to date provided the basis for the safety underpinning of the mitigation effort. Furthermore, the finding (supported by the simulated waste studies) that about 80 percent of the original complexant added to tank 101-SY has been further oxidized to less reactive products, such as sodium formate and oxalate, will be broadly applicable to all other tanks containing complexing agents. This finding is especially useful with respect to its implications to the organic program and to making a determination of waste compatibility associated with future transfers for purposes of waste treatability.<br><br>Solubility measurement of nitrous oxide in simulated waste, as a function of pressure, indicates that solubility of nitrous oxide in waste makes a negligible contribution to gas retention.<br><br>Subcritical wet oxidation was shown to be an effective means of destroying organics using simulated tank 101-SY waste feeds.<br><br>References: Schulz and Strachan 1992. |
| Analytical (assay) development | Methods have been developed for taking physical property measurements of viscous radioactive waste and for identifying complexant degradation fragments in complex synthetic and actual waste solutions. |
| Tank operations | Air lances were removed from tank 101-SY to eliminate potential spark sources and to free up additional risers for other instruments. |

| Information | Preliminary conclusion or result |
|---|---|
| Issue resolution strategy | A report on USQ resolution was issued containing extensive background material on tank 101-SY (Simpson et al. 1992). This document, and a technical support document associated with it (Anantatmula 1992), provided accident consequences criteria and more accurately defined those program elements required for the resolution of the USQ. |

[1]GOTH is a computer code developed by Numerical Applications, Inc.
[2]TEMPEST is a computer code developed by Battelle/Pacific Northwest Laboratory.

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# 3.0 FERROCYANIDE-CONTAINING TANKS

## 3.1 INTRODUCTION

A requirement during the 1950's for additional storage capacity in single-shell tanks (SSTs) for wastes from production activities led to a need to remove radiocesium from otherwise dilute wastes prior to soil column disposal. To accommodate the need for additional radioactive waste storage capacity, the Hanford Site operating contractor used the "ferrocyanide scavenging" process to convert soluble radiocesium present in stored wastes to an insoluble species, thus allowing disposal of additional aqueous wastes to a soil column (cribs) without exceeding specifications for release of radionuclides. The use of several flow sheets for radiocesium scavenging resulted in tons of a ferrocyanide waste having a variety of compositions.

A ferrocyanide reaction in an SST was the worse case scenario analyzed in the Hanford Defense Waste Environmental Impact Statement (issued as a draft in 1986 and in final form in 1987 [DOE 1987]). The consequences of the accident were challenged by the General Accounting Office in 1990, so the accident was not bounding (Peach 1990). This led to the declaration of a USQ in October 1990 on the ferrocyanide tanks. These tanks had already been placed on a watchlist in May of 1990.

Because of observed thermal reactivity of ferrocyanides with nitrate and the resulting concerns about the safe storage of these wastes, WHC established an aggressive multiple participant program to evaluate the actual risk from continued storage of ferrocyanide-containing waste in Hanford Site SSTs. Major program participants include the following:

| Program participants | Program role |
|---|---|
| Westinghouse Hanford Company | Program management, engineering studies, safety and environmental analysis, preparation of waste simulants, and waste characterization |
| Pacific Northwest Laboratory | Applied R&D on waste energetics, ferrocyanide reaction kinetics, analytical methods development, waste aging studies, and waste characterization support |
| Fauske and Associates | Calorimetry, propagation studies, and safety analysis support |
| Los Alamos National Laboratory | Calorimetry and explosive testing |

## 3.2 SUMMARY FISCAL YEAR 1992

Much progress was made this fiscal year toward putting the risk from the ferrocyanide safety issue into perspective. The starting point for these efforts were two documents in which WHC evaluated its understanding of the ferrocyanide issue (Postma et al. 1991 and Grigsby et al. 1991). In these documents, a strategy for issue closure required (1) demonstrating the absence of a requisite inventory of ferrocyanide in any given tank (intrinsic safety); (2) proving the concentration of ferrocyanide in any given tank was too dilute to prove a threat (passive safety); or (3) controlling the temperature and moisture content, which would provide a continuing assurance of safety (controlled safety). Additional technical background information on this issue is available in a report by the PNL Science Panel (Burger et al. 1991), an oversight group, and in a report written by the DOE Technical Advisory Panel (Kazimi et al. 1992).

The results of tank thermal analyses, kinetics and energetics studies on simulants that duplicated actual plant flow sheets, and characterization of actual waste are beginning to clearly demonstrate that the ferrocyanide-containing tanks appear to be safer then previously thought. Subject to an anticipation of no surprises from FY 1993 applied R&D and characterization efforts, mitigation or remediation of ferrocyanide-containing tanks is not believed necessary to resolve the USQ.

The following summarizes the findings.

- Ferrocyanide waste appears to contain at least 50 percent water, a condition that will prevent heating of the waste and preclude propagation of a ferrocyanide nitrate-nitrite reaction.

- Several of the flowsheets (U Plant and T Plant), representing most of the of the inventory (e.g., ~80 percent), are diluted with enough inert materials that they are nonreactive when heated, even when dry.

- Available instrumentation indicates that ferrocyanide tank temperatures are low and have shown a continuous drop as expected from radionuclide decay.

- Analysis of actual tank samples suggests that even in waste created by the most reactive (In Farm) flowsheet, in-tank waste aging has occurred to significantly lower fuel values (reactivity), to a level comparable with the U Plant flowsheets.

The key FY 1992 achievements are listed below:

- Determined the energetics of ferrocyanide flowsheet simulants for processes used at the Hanford Site

- Obtained cores from tanks 112-C and 109-C, and obtained detailed waste characterization results from tank 112-C

- Completed extensive hot spot modeling and other safety analysis related work

- Completed initial evaluation of the use of infrared scanning techniques for measuring in-tank surface temperatures

- Performed extensive thermocouple repair and installed new thermocouples.

A more extensive summary of accomplishments is tabulated below.

| Information | Preliminary conclusion or result |
|---|---|
| Determined U Plant flowsheet and a very similar T Plant flowsheet simulant energetics (this flowsheet represents 80 percent of the ferrocyanide tank inventory) | Waste simulants prepared from the U Plant flowsheets contain sufficient concentrations of inorganic diluents that the effective concentration of ferrocyanide salts (dry weight basis) is only about 2 percent. Such simulants are also wet (60 percent water), even after centrifugation for 30 gravity years. When dried, the simulants do not exhibit propagating or explosive behavior when heated to temperatures well above 200 °C. |
| Determined In Farm flowsheet simulant energetics | Simulants prepared from the In Farm flowsheets contain sufficient concentration of ferrocyanide salts that the effective concentration of ferrocyanide salts (dry weight basis) is about 18-20 percent. These simulants are also wet (50 percent water), even after centrifugation for 30 gravity years. When completely dry, these materials do exhibit propagating or explosive behavior when heated to temperatures above 200 °C. However, the energy of reaction is only a third of that predicted on the basis of thermodynamic considerations. Propagation rates are slow (~5-10 cm/min.), the equivalent of a "slow burn." Addition of as little as 12 percent moisture to the dry simulant precludes propagation. |
| C Tank Farm characterization results | Analysis of actual cores taken from tanks 112-C and 109-C strongly suggest that the actual waste has either been degraded or diluted over its 30-year storage period. The results of differential scanning calorimetry, thermal gravimetric analysis, and some adiabatic calorimetry show energies of reaction that are lower than that of the U Plant flowsheet (e.g., the dry materials cannot propagate or explode at temperatures well above 200 °C). |

| Information | Preliminary conclusion or result |
|---|---|
| Hot spot modeling | Extensive modeling of tank 104-BY (the tank with the greatest "inventory" of ferrocyanide salts and the greatest amount of overlying saltcake insulator) demonstrated that it would require an unreasonable enrichment of 150 to 500 times average tank concentration of the heat-producing materials needed to create a credible hot spot. In addition, detailed analysis based on calorimetric results, using worse case In Farm flowsheet energetics, also demonstrates that a hot spot is an unreasonable event.<br><br>• The heat loads for seven tanks were more accurately recalculated. All values were significantly lower then those reported previously. |
| Other results | The potential usefulness of infrared scanning as a means of mapping surface waste temperatures was demonstrated. This provides an alternative surveillance tool for measuring the surface temperature of the waste in ferrocyanide tanks. |
| Analytical (assay) development | Problems with total cyanide assay have led to an intensive effort to remedy the problems with this key assay. Detailed screening efforts were also completed to identify assays that would quantify the individual ferrocyanide species in actual tank waste. Two promising methods that will be explored further in FY 1993 are (1) fourier transform and (2) infrared and high performance liquid chromatography analysis.<br><br>• Preliminary neutron probe scans and data analyses show that accurate in-tank moisture measurements are possible by modifying existing probes. This work is funded in FY 1993. |

| Information | Preliminary conclusion or result |
|---|---|
| Tank operations | • Performed extensive thermocouple repair (e.g., 26 thermocouples repaired and 11 switches replaced), installed new thermocouples (104-BY, 110-BY, 109-C, and 112-C), and significantly upgraded the data acquisition systems associated with temperature measurement in ferrocyanide Watchlist tanks. The new thermocouple tree temperature agrees well with data obtained from the existing trees.<br>• Completed the continuous temperature monitoring system in BY, T, and TX Tank Farms; 14 tanks are now monitored continuously. As a side effect of this effort, extensive data scatter that characterized manual data has been eliminated.<br>• Initiated extensive gas sampling of tank dome vapor space. Initial sampling results from tanks 104-BY, 110-BY, 109-C, and 112-C indicate that the ferrocyanide tanks tested to date contain neither hazardous nor flammable gases in concentrations that would put the operators or environment at risk. |
| Waste aging | Aging of sodium nickel ferrocyanide under high pH conditions leads to waste hydrolysis. Investigation of chemical and radiolytic aging of ferrocyanide wastes continues in FY 1993. |

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# 4.0 ORGANIC TANKS

## 4.1 INTRODUCTION

In 1989, the presence of organic chemicals in Hanford Site waste tanks became an issue for reevaluation as information became available on the September 29, 1957, deflagration of a waste tank in Kyshtym, U.S.S.R. (IAEA 1989). The Russian tank event occurred because cooling was disrupted, the aqueous solutions of acetate containing salts were evaporated to dryness by radio-decay heat, and the mixture of oxidizing salts and organic chemical waste self-heated to deflagration-initiating temperatures. The constituents in the tank that caused this incident were sodium nitrate and sodium nitrite mixed with sodium acetate. The chemical safety issue associated with the organic tanks is that, in a mixture of organic waste components with oxidizing salts (e.g., sodium nitrate and sodium nitrite) and a low moisture content, there is a possibility that hazardous exothermic reactions may occur.

A screening study was conducted at the Hanford Site in 1989. Twenty-six tests were performed as a preliminary study of the reactivity of mixtures containing various proportions of sodium acetate, sodium nitrate/sodium nitrite, and diluents. The results were used to define an upper limit for acceptable concentration of total organic carbon (TOC) constituents in the waste. The limit was defined as 10% organic equivalent weight to sodium acetate, which corresponds to 3% TOC. The results of this study, along with process engineering knowledge, form the basis for placing waste tanks on the organic tanks watchlist. Process engineering knowledge involves evaluating process flow sheets, the waste inventory database, and other plant records. Eight SSTs were identified as possibly having an organic content in excess of 3% TOC threshold concentration and were placed on the list. (One of these eight tanks is also listed on the ferrocyanide watchlist and two of the eight tanks are listed on the flammable gas watchlist.)

Process engineering knowledge of waste composition was used for assigning the eight tanks listed to the watchlist, rather then actual assay results, because of limitations in the historical records. High concentrations of organic compounds have been found in these eight SSTs (from tank transfer and flow sheet records and limited analytical data). Although some of the DSTs have high concentrations of organic materials, they were not included in the watchlist because they were known to have high moisture contents, which would preclude a propagating reaction. The exact concentrations of organic materials in these SSTs are not yet accurately known. These tanks are listed because they may contain organic chemicals in quantities sufficient to sustain a reaction that may result in the release of high-activity waste.

An overview report on the information and existing science underlying the organic issue is being finalized by the PNL science panel (a technical oversight committee).

Planned program participants include the following:

| Program participant | Program role |
|---|---|
| Westinghouse Hanford Company | Program management, waste reactivity modeling, waste tank monitoring and characterization, engineering studies, records analysis (flow sheet and transfer), safety and environmental analysis, waste characterization, and actual radwaste degradation studies. |
| Pacific Northwest Laboratory | Applied R&D on waste system physical modeling waste energetics, waste concentration mechanisms, analytical methods development, waste aging studies, and waste characterization support |
| U.S. Bureau of Mines | Energetics study on organic waste surrogate compounds |
| U.S. Department of Energy and/or University Laboratory | Nonradioactive chemically induced chemical degradation studies on simulants |

## 4.2 SUMMARY FISCAL YEAR 1992

A significant portion of the activities of the organic program has dealt with program planning and the theoretical evaluation of the potential energetics of nitrate-nitrite organic waste mixtures. The organic program was only minimally funded last fiscal year. A summary of accomplishments is listed below:

- Developed a preliminary strategy for issue closure
- Estimated the theoretical energetics of organic-nitrate-nitrite waste reactions as a function of the structure of organic materials
- Reported on potential organic concentration mechanisms
- Defined a detailed test sequence (to be carried out by the U.S. Bureau of Mines) to determine actual organic waste-related chemical energetics, as a first step in defining a basis for the organic watchlist specification.

A more extensive summary of accomplishments is tabulated below.

| Information | Preliminary conclusion or result |
|---|---|
| Development of a strategy for issue closure | Extensive program planning using the Science Applications International Corporation (SAIC) logic has been initiated to define the most reasonable route to gaining the necessary and sufficient information to deal with the organic issue. Significant emphasis on defining R&D and analytical methods development needs have been completed and will become part of the program plan. The overall R&D strategy was presented to the Technical Advisory Panel. |
| Identification of potential organic concentration mechanisms. | PNL completed and published a detailed analysis evaluating potential mechanisms by which organic materials might become concentrated in Hanford Site tanks (Gerber et al. 1992). This effort parallels an effort that was initiated to identify aging (e.g., degradation) mechanisms for organic waste in tanks. |
| Theoretical energetics estimates of organic-nitrate-nitrite waste reactions | Studies conducted by WHC suggest that the existing specification for organic watchlist tanks (3% TOC - dry weight basis) was not conservative. Instead it was suggested that 0.43-1.05% TOC will not be dangerously exothermic in the absence of inerting agents (such as water). The 0.43% represents a hydrocarbon fuel, such as normal paraffin hydrocarbon (also sodium nickel ferrocyanide) or a hydrocarbon-based surfactant, while 1.05% represents a material-like sodium citric acid. (These were considered by staff to be nondangerous levels.) |
| Energetics testing | A study was defined that detailed a parametrically designed test sequence, to be carried out by the U.S. Bureau of Mines in support of a determination of the reactivity for a spectrum of organic substrates. This is the first step in more precisely defining the actual risk from organic chemicals and nitrate-nitrite systems. The test will be part of the FY 1993 program. |

| Information | Preliminary conclusion or result |
|---|---|
| Other efforts | • A report was received from British Nuclear Fuels Limited on alternative methods for mixing wastes in organic SSTs (McKeon et al. 1992).<br>• A literature search (focusing on North American literature) for analytical methods for organic assays that can be used in a radioactive waste environments was completed. A report will be published during FY 1993.<br>• A procurement package was prepared for \$800M high-resolution mass spectrometer systems to support precise structural analysis of organic materials in core samples. |

# 5.0 TANK VAPOR CONCERNS

## 5.1 INTRODUCTION

The realization by WHC staff that periodic and unpredictable releases of tank vapors in and around the tank farm facilities are more prevalent than was previously thought requires aggressive action to correct this problem. Seventeen workers between 1987 and the present have claimed to have been affected or irritated by such vapors. WHC has taken a conservative approach to worker protection, placing the C, BX, and BY Tank Farms on "required" fresh air respirators. This added worker protection results in a slowing of all work and can cause other safety concerns (e.g., heat fatigue or decreased visibility). The existence of safety concerns related to noxious vapors, coupled with our concern for worker safety, could slow or interfere with the following:

- The orderly planned short-term closure of waste tank safety problems
- The longer-term remediation of these tanks
- The orderly remediation of solid and liquid waste sites.

This led to the need for preparing an organized integrated strategy for dealing with the tank vapor issue.

Plant operators and other WHC staff members have periodically identified the presence of noxious vapors released near or from some SSTs and, on occasion, DSTs at the Hanford Site. On rare occasions workers have requested first aid as a result of breathing these vapors. These occurrences do not appear to be episodic in nature. The identification of the presence of possible noxious gases from the tanks has been made both by smell and with industrial safety general tank vapor monitoring equipment. Gas releases have taken place under a variety of circumstances ranging from (1) their temporary presence during the performance of routine monitoring and preventative maintenance duties external to the tanks and (2) incidents related to an actual penetration of the tank systems.

Major program participants include the following:

| Program participants | Program role |
|---|---|
| Westinghouse Hanford Company | Program management, industrial safety support, engineering studies, safety analysis, preparation of waste simulants, and waste characterization |
| Pacific Northwest Laboratory | Technical consulting, aerosol analysis, and waste characterization and gas analysis support |
| Oak Ridge National Laboratory | Technical consulting and gas analysis support |
| Sandia National Laboratory | Technical consulting and gas analysis support |
| Mr. Mike Story, Northwest Instruments Systems, Inc. | Technical oversight and support |
| Hanford Environmental Health Foundation | Industrial safety and health support |
| Oregon Graduate Institute | Gas analyses |

## 5.2 SUMMARY FISCAL YEAR 1992

A significant portion of the activities of the tank vapors program has dealt with program planning, responding to a DOE "type B" investigation related in response to the vapor exposures, and preparing for validated sampling of 103-C in response to complaints of odors associated with that tank. No less important has been the work aimed at finding a means to allow operators a safe reprieve from fresh air respirator use in and around the SSTs in the C, BX, and BY Tank Farms. This program was initially funded in the last quarter of FY 1992. A full-time program manager was hired to run the program.

The key accomplishments in FY 1992 are listed below:

- Initiated development of a strategy for issue closure
- Initiated development of validated gas space sampling techniques for tank 103-C
- Initiated development of an alarmed tank work space monitoring system to allow operators to come off of fresh air
- Initiated the noxious odor advisory system (NOAS) operator alert warning system.

A more extensive summary of accomplishments is tabulated below.

| Information | Preliminary conclusion or result |
|---|---|
| Develop a strategy for issue closure | Extensive program planning using the SAIC logic has been initiated to define the most reasonable route to gaining the necessary and sufficient information to deal with the tank vapor issue. Significant emphasis on defining R&D associated with valid sampling, area monitoring, and work space monitoring, as well as analytical methods development needs, have been completed and will become part of the tank vapor program plan.<br><br>• Assembled a multidisciplinary "peer" vapor sampling team with members from WHC, PNL, Oak Ridge National Laboratory, Sandia National Laboratory, Ames Laboratory, Northwest Instruments Systems, Inc., and the Oregon Graduate Institute. |
| Develop validated gas space sampling techniques | • Extensive efforts initiated in FY 1992 were aimed at finding ways to accurately determine the vapor composition in tank 103-C. Although many techniques exist for the accurate sampling and monitoring of ambient air (work space monitoring), these methods have not been validated for the conditions found in the tank. The combination of high hydrocarbon concentrations, the presence of a saturated water environment, and the presence of a variety of other gases, including high concentration of ammonia, make characterizing the tank vapors difficult and monitoring the tank dome contents with existing industrial equipment indefensible.<br><br>• Initial phase "0" sampling to tank 103-C was completed, providing initial data on the tank vapor contents and a start in method validation.<br><br>• The design of a trailer housed automated vapor sampling apparatus was completed. |

| Information | Preliminary conclusion or result |
|---|---|
| Develop a tank work space monitoring system to allow operators to come off of fresh air | Initial evaluations of alternative systems have been explored for alarmed monitoring of the effluents from 103-C (e.g., at the end of pipe-high-efficiency particulate air or activated carbon filters) and/or for fast response time alarmed aerial monitors. Such devices would, in conjunction with the operator's sense of smell, provide an early warning of a gas release. Use of a "5 minute" fresh air pack when an alarm is sounded would provide safe up-wind means of evacuation from the tank farm. Fresh air would still be required for tank intrusive activities, as defined by the plant operating safety documents. |
| Develop the NOAS operator alert warning system | NOAS (pronounced "nose") is a tank farm air quality indicator system that creates a proactive administrative control system to protect the worker. It would implement a system for orderly and timely investigation of reports of noxious odors in the tank farms. A key benefit of the NOAS system is use of an in-tank farm display technique that facilitates clear communication of hazardous vapor conditions to the workers in real time. |

# 6.0 HIGH-HEAT TANK

## 6.1 INTRODUCTION

Between 1969 and 1971, high-heat sludge was water-sluiced from aging waste stored in SSTs in the A and AX Tank Farms to recover $^{137}Cs$ and $^{90}Sr$. The sludge washing/decanting step in this process did not function as planned and resulted in the transfer of strontium-rich solids to SSTs 105-C and 106-C. The tanks now contain as much as 41,639 and 181,699 L (11,000 and 48,000 gal) of drainable liquids, and 567,810 and 745,723 L (150,000 and 197,000 gal) of sludge respectively (there is no saltcake in either tank). As of 1988, the waste contained in tank 105-C was estimated to generate heat at the rate of between 12,100 and 52,630 Btu/h, with a best estimate of 52,000 Btu/h. For tank 106-C, the rate of heat generation was estimated to range between 61,550 and 176,000 Btu/h, with a best estimate of 158,000 Btu/h. At issue are concerns both about the structural integrity of the concrete liners of tank 106-SY and about the possibility of future leakage of waste from this SST, to which water must be added to maintain thermal control.

In mid-1971, when waste temperatures in excess of 99 °C (210 °F) were observed in tank 106-C, both tank 105-C and tank 106-C were immediately placed on shared forced air ventilation. Since mid-1971, water has been added periodically to both tanks to (1) cover the sludge solids, (2) promote heat transfer and evaporative cooling, and (3) permit accurate in-tank liquid level measurements using supplier's gauges. Both tanks are considered to be sound (nonleaking) and were placed on inactive status in 1979. Over the last 7 years, the liquid added to these tanks has averaged approximately 4,542 L (1,200 gal)/month for tank 105-C and 29,148 L (7,700 gal)/month for tank 106-C. When the decrease in the liquid level in the tank reaches a pre-established level (believed to be caused by evaporation only), water is then added to reestablish a maximum liquid level.

In January 1991, in accordance with the *National Defense Authorization Act for Fiscal Year 1991*, Public Law 101-510, Section 3137 (Wyden Amendment) tank 106-C was identified as a high-level waste tank at the Hanford Site that "may have a serious potential for release of high-level waste due to uncontrolled increases of temperature or pressure." Tank 106-C was placed on the watchlist because, if drainable liquid was not maintained in the tank (even if the tank should leak), an uncontrolled increase in temperature could occur. This could result in structural damage to the tank's concrete, with a potential subsequent release of high-level waste. To prevent waste temperatures in excess of the 148 °C (300 °F) operating limit, cooling is currently accomplished by water evaporation, using active filtered air ventilation system. Water content is supplemented by periodic additions to maintain a liquid cover over the sludge for enhanced thermal conductivity. The basis for the safety issue is the need to maintain drainable liquid by periodic raw water additions to control the temperature.

Tank 105-C, the only other high-heat generating tank at the Hanford Site that has periodic cooling water added (although in much lesser amounts than for tank 106-C), is not expected to require cooling water additions, even if the tank were to dry out completely. For that reason, the tank was not identified as a watchlist tank, even though additional documentation and instrumentation have been recommended before terminating water additions.

A means must be provided to resolve this safety issue. The following five alternatives are being evaluated: (1) reduce the volume of cooling liquid in the tank to less than the interstitial holdup in the sludge (i.e., nondrainable liquid); (2) determine if the tank can safely withstand higher concrete temperatures if only intermittent ventilation were used as cooling; (3) provide alternative cooling methods other than forced ventilation supplemented with liquid additions; (4) reduce the heat source in the tank sufficiently (retrieved) to eliminate the need for any drainable liquid if the cooling liquid cannot be reduced to below drainable due to temperature constraints; or (5) contain the drainable liquid within the tank (barriers) so that it cannot leak out. The fourth alternative (removal of the waste) is being aggressively pursued both as the permanent solution to the safety issue as well as to support present disposal plans. Preliminary evaluations of alternative five (barriers under the tank) indicate that it would be extremely expensive and difficult to prove containment. Alternatives one through three are considered interim "fixes" until retrieval of the waste occurs.

Major program participants include the following:

| Program participants | Program role |
|---|---|
| Westinghouse Hanford Company | Program management, engineering studies, safety and environmental analysis, preparation of waste simulants, and waste characterization |
| Pacific Northwest Laboratory | Waste characterization and other technical support |

## 6.2 SUMMARY FISCAL YEAR 1992

A significant portion of the activities of the high-heat tank program, in part as an extension of previous program activities, has dealt with the following:

- Quantifying the absolute minimum amount of cooling liquid required to control the temperatures in tanks 105-C and 106-C
- Determining process test for stopping water additions to tank 105-C.

The key accomplishments in FY 1992 are listed below:

- Initiated development of a strategy for issue closure
- Determined a process test for stopping water additions to tank 105-C
- Initiated tank 106-C thermal model development.

A more extensive summary of accomplishments is tabulated below.

| Information | Preliminary conclusion or result |
|---|---|
| Develop a strategy for issue closure | Extensive program planning using the SAIC logic has been completed to define the most reasonable route for resolving the high-heat tank issue. Significant emphasis on modeling the behavior of 106-SY and exploration of methods for the retrieval of waste from 106-C have been the primary program focus. |
| Prepare a strategy for minimizing water addition to tank 106-C | Extensive planning, including engineering analysis and thermal modeling work, was initiated to support strategies for minimizing the water addition to tank 106-C. |
| Scope out process test for stopping water additions to tank 105-C | Providing the adequate documentation and monitoring to allow termination of water additions to tank 105-C will provide useful data to determine whether water control in tank 106-C is a possible mitigation method. This work, which was initiated in FY 1992, will be completed in FY 1993. |
| Tank 106-C thermal model development | The model is expected to project the minimum liquid level needed to maintain the waste temperature below the maximum allowable limit. The model will be verified by data from a process test on tank 105-C. This work, which was initiated in FY 1992, will be completed in FY 1993. |
| Tank 106-C structural model development | An updated structural analysis has been developed for 106-C. This model will take the output from the thermal analysis and confirm that structural integrity will be maintained for the foreseeable future. The model analyzes estimated past thermal, dead and live loads from 1947 to the present, as well as projected thermal, dead and live and seismic loads until the longest estimated retrieval date (approximately 2010). This model addresses both thermal cycling and extended elevated temperatures on the reinforced concrete. This work, which was initiated in FY 1992, will be completed in FY 1993. (This work is not funded by the Waste Tank Safety Program.) |

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